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(54) OXYMETHYLENE POLYMERS AND COPOLYMERS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, residing at 1 River Road, 5 Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to cured oxymethylene polymers or copolymers, to heat-curable oxymethylene polymer or copolymer compositions for preparing said polymers or copolymers and to a process for producing said cured polymers or copolymers; these cured materials have improved resistance to meltflow and decomposition by electrical arcs. They are useful as electrical insulators and circuit breaker liners, for example.

Linear oxymethylene polymers (polyformaldehydes) and their copolymers are known in the art. These polymers have limited applicability because of their instability and other undesirable properties. These oxymethylene polymers melt at lower temperatures and frequently depolymerize at elevated temperatures to yield volatile formaldehyde gases which are irritating to persons in the vicinity.

A number of ways for improving the properties of oxymethylene polymers and copolymers have been described in the literature, for example, in United States Patent No. 2,768,994—MacDonald. The polymer treated by the method of this patent is, however, soluble and fusible and for some purposes a product which is less thermoplastic, and more resistant to solvents is desired.

Polyoxymethylene have been improved by crosslinking in accordance with United States Patent 3,215,671—Melby, which is directed to preparing crosslinked polyoxymethylene by exposing, to ionizing radiation, a polyoxymethylene having intimately mixed or dispersed therein from 0.5 to 20%, by weight, of selected polyunsaturated compounds. It is further stated that crosslink-

ing is developed by exposing to ultraviolet light, a mixture of polyoxymethylene and poly-unsaturated compound containing a photoinitiator. It is further stated in the Melby patent that peroxide catalysts are not useful in effecting crosslinking of polyoxymethylenes.

It has been discovered that when oxy-methylene polymers and copolymers are admixed with triallylcyanurate and then dicumyl peroxide added, and the resultant mixture heat-cured, a crosslinked material results which crosslinking would be entirely unexpected in view of the disclosure in the Melby patent. 60

The present invention thus provides a heat-curable composition comprising, by weight, a mixture of an oxymethylene polymer or copolymer, and, per 100 parts of polymer or copolymer, 1 to 50 parts triallylcyanurate and 0.5 to 10 parts dicumyl peroxide. 65 70

The present invention also provides a process for producing a cured oxymethylene polymer or copolymer, comprising heating a heat-curable composition according to the present invention to a temperature of 165°—200°C. to decompose the dicumyl peroxide and cure the composition.

The oxymethylene polymers suitable as starting materials in the process of this invention and which are mixed with triallylcyanurate and dicumyl peroxide are those having oxymethylene chains of at least 100 oxymethylene units in length. All oxymethylenes polymers of this length and over can be employed whether the chains are terminated by ester groups, methyl groups, or other groups. Thus, there may be employed α -polyoxymethylenes, β -polyoxymethylenes, and the higher molecular weight polyoxymethylenes such as eu-polyoxymethylene, as described by J. F. Walker (formaldehyde) second edition, Rheinhold Publishing Corporation, 1953, pages 1-9. The production of the oxymethylene polymers employed in the Examples given hereinafter is described in United States Patent 3,215,671.

The oxymethylene copolymers useful in

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producing the arc resistant compositions of this invention are suitably those copolymers containing polyoxymethylene groups joined by alkylene oxide units and can contain from 5 0.1 to 15 mole % of the alkylene oxide units, i.e., they are formaldehyde-alkylene oxide copolymers. These copolymers are prepared in accordance with the process of United States Patent 3,027,352.

10 The amount of triallylcyanurate employed in the process of this invention is not narrowly critical and can range from 1 to 50 (preferably 1 to 40) parts, by weight, per 15 100 parts, by weight, of the oxymethylene polymer or copolymer.

15 The amount of dicumyl peroxide employed in the process of this invention is also not narrowly critical and can range from 0.5 to 20 10 parts, by weight, of dicumyl peroxide for each 100 parts, by weight, of the oxymethylene polymer or copolymer.

20 The cured product of this invention may be produced in such a way that the oxymethylene polymer or copolymer is placed on a roll mill which is heated to 165°C—

25 175°C and the triallylcyanurate added with 30 35 40 45 50 milling until an intimate mixture is obtained; the mixture is then cooled to about 130°C—150°C and the dicumyl peroxide added slowly while the mixture is milled to give an intimate mixture of the triallylcyanurate, oxymethylene polymer or copolymer and the dicumyl peroxide, the mixture is then placed in a mold and heated at 165°C to 200°C for about 5 to 90 minutes, whereby the material becomes cured, i.e. cross-linked.

40 As was indicated above, the temperature at which the process described in the preceding paragraph is conducted must be controlled. The milling of the oxymethylene polymers or copolymers and the triallylcyanurate can be conducted at temperatures from 150°C to about 200°C, to ensure the 45 intimate mixing of these materials. The temperature at which the dicumyl peroxide is added on the roll mill must be controlled so that there is no premature decomposition of the dicumyl peroxide with resulting cross-linking of the polymer on the roll mill.

55 One can also employ in producing the compositions of this invention, various fillers such as glass flock, powdered glass, asbestos, and the like. The amount of filler employed in the compositions of this invention is not narrowly critical and can range from 1 part (suitably 10 parts) filler per 100 parts polymer to 100 parts filler, by weight, per 100 parts, by weight, of the oxymethylene polymer or copolymer.

60 The following Examples serve to further illustrate this invention. All parts are, by weight, unless otherwise expressly set forth.

EXAMPLE I

65 150 Parts of a copolymer of formaldehyde

and ethylene oxide and 50 parts of oxymethylene homopolymer were added to a two-roll differential speed roll mill and which had been heated at 170°C and the homopolymer and copolymer mixed by milling. Triallylcyanurate (40 parts) was then added and the mixture continued to be milled until an intimate dispersion of the triallylcyanurate and the oxymethylene polymers were obtained. The mixture was then cooled on the roll mill to about 130°C to 145°C and dicumyl peroxide (1 part) was added with milling to give an intimate mixture. The mixture was then preheated and pressed at 165°C for 15 minutes, yielding a sheet having a tensile strength at 200°C of 7 pounds per square inch and an elongation of 103%. This crosslinked polymer, when heated to 200°C, was rubbery. A sample of the mixture which did not contain dicumyl peroxide nor triallylcyanurate melted when heated to 200°C and had no tensile strength at this temperature.

EXAMPLE 2

A copolymer of formaldehyde with ethylene oxide blended with 20 weight % of glass fibre was placed on a two-roll differential speed mill which was heated to 170°C and the mixture milled and triallylcyanurate (20 parts) added with milling to give an intimate dispersion.

The rolls were then cooled to about 140°C to 150°C and 0.5 parts of dicumyl peroxide added with milling to yield an intimate dispersion of the copolymer, triallylcyanurate, glass fibres, and dicumyl peroxide. This material was then heated at 165°C for 30 minutes under 1000 psi gauge pressure to yield a crosslinked material having a thickness of 30 mils and a tensile strength of 25 lbs. per square inch and an elongation of 100%, both when measured at 200°C.

A portion of the above mixture of copolymer and glass fibers which contained no triallylcyanurate nor dicumyl peroxide was treated in the same manner and when heated to 200°C, it melted and no tensile test could be conducted. This indicates that the material was not crosslinked.

WHAT WE CLAIM IS:—

1. A heat-curable composition comprising, by weight, a mixture of an oxymethylene polymer or copolymer, and, per 100 parts of polymer or copolymer, 1 to 50 parts triallylcyanurate and 0.5 to 10 parts dicumyl peroxide.

2. A composition according to Claim 1, wherein the composition additionally contains 1 to 100 parts of a filler per 100 parts of polymer or copolymer.

3. A composition according to Claim 2, wherein the filler is glass fibre.

4. A composition according to Claim 1

substantially as herein described with reference to Example 1 or 2.

5. A process for producing a cured oxy-methylene polymer or copolymer, comprising

5 heating a heat-curable composition as claimed in any one of Claims 1 to 4 to a temperature of 165°—200°C. to decompose the dicumyl peroxide and cure the composition.

10 6. A process according to Claim 5 substantially as herein described with reference to Example 1 or 2.

7. A cured polymer or copolymer obtained by the process as claimed in Claim 5 or 6.

8. An electrical insulator or circuit breaker liner constituted by a polymer or copolymer as claimed in Claim 7.

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